

8.0 POLLUTION PREVENTION PRACTICES AND WASTEWATER TREATMENT TECHNOLOGIES

This section presents an overview of pollution prevention practices and wastewater treatment technologies in the MP&M industry. Section 8.1 describes pollution prevention practices, Section 8.2 describes technologies used for the preliminary treatment of waste streams, and Section 8.3 describes end-of-pipe wastewater treatment and sludge dewatering technologies. This section discusses the most prevalent technologies in place at MP&M facilities, including all the technologies used as a basis for the MP&M effluent guidelines. However, additional technologies may be applicable for some MP&M facilities, depending on the waste streams generated. Additionally, not all technologies discussed in this section are applicable to all MP&M sites; the technology applicability is driven by the processes performed and waste streams generated on site.

8.1 Pollution Prevention Practices

Pollution prevention practices reduce the generation or discharge of pollutants and therefore potentially reduce treatment or disposal costs. Typical pollution prevention practices include reducing water use, extending the life of process bath constituents, or adding recycling or reuse technologies. This section divides pollution prevention practices into three categories. Section 8.1.1 discusses flow reduction practices, Section 8.1.2 discusses in-process pollution prevention technologies, and Section 8.1.3 describes additional methods of pollution prevention.

8.1.1 Flow Reduction Practices

Flow reduction practices are applied to process baths or rinses to reduce the amount of wastewater discharged. Flow reduction practices consist of optimizing rinse tank design and configuration and installing flow reduction technologies such as flow restrictors or timers. The following sections discuss flow reduction practices in greater detail.

8.1.1.1 Rinse Tank Design and Innovative Configurations

Rinsing follows many MP&M unit operations to remove dirt, oil, or chemicals (i.e., drag-out) remaining on parts or racks from a previous unit operation. Rinsing improves the quality of the surface finishing process and prevents the contamination of subsequent process baths. Rinse tank design and rinsing configuration are important factors influencing water usage. The key objectives of optimal rinse tank design are to quickly remove drag-out from the part and to disperse the drag-out throughout the rinse tank.

The MP&M industry uses various rinsing configurations. The use of single overflow rinse tanks following each process tank is the most inefficient use of rinse water. Multiple rinse tanks connected in series (i.e., cascade rinsing) reduce the water needs of a given rinsing operation by one or more orders of magnitude (i.e., less water is needed to achieve the same rinsing criterion). Spray rinsing can also be used to reduce water use requirements, but the

achievable percent reduction of water use is usually less than for countercurrent cascade rinses. A description of some of the common rinse types is provided below.

Cascade rinsing

Cascade rinsing is a method of reusing rinse water. Rinse water from one rinsing operation is plumbed to another, less critical rinsing operation before being discharged to treatment. Some rinse waters acquire chemical properties, such as low pH, that make them desirable for reuse in other rinse systems. For example, an acid treatment rinse may be plumbed to an alkaline treatment rinse, providing both drag-out removal and neutralization.

Countercurrent Cascade Rinsing

Countercurrent cascade rinsing refers to a series of consecutive rinse tanks which are plumbed to cause water to flow from one tank to another in the direction opposite of the work flow. Fresh water flows into the rinse tank located farthest from the process tank and overflows, in turn, to the rinse tanks closer to the process tank. This technique is termed countercurrent rinsing, because the work piece and the rinse water move in opposite directions. Over time, the first rinse becomes contaminated with drag-out and reaches a stable concentration which is lower than the process solution. The second rinse stabilizes at a lower concentration, which enables less rinse water to be used than if only one rinse tank were in place. Increasing the number of countercurrent cascade rinse tanks (three-stage, four-stage, etc.), reduces the amount of water needed to adequately remove the process solution. Figure 8-1 shows the application of countercurrent cascade rinsing.

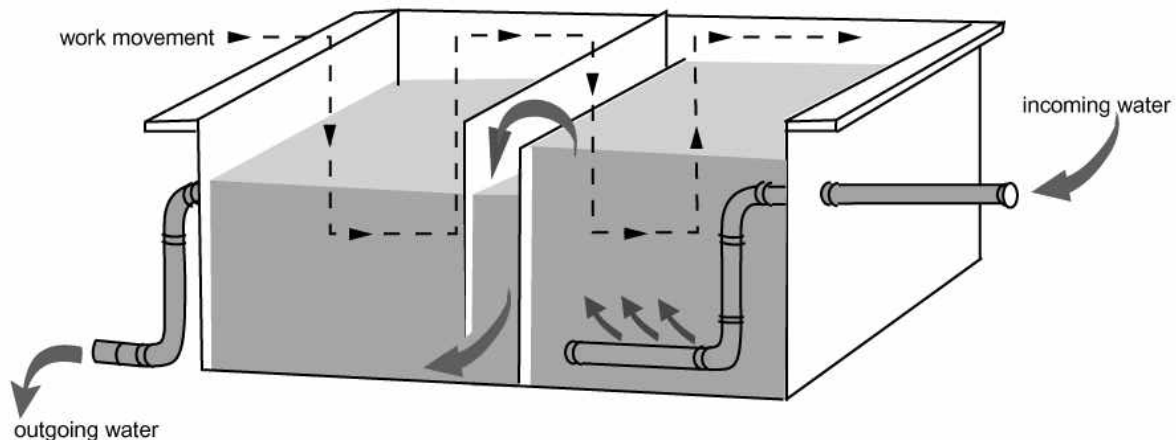


Figure 8-1. Countercurrent Cascade Rinsing

The rinse rate needed to adequately dilute drag-out depends on the concentration of process chemicals in the drag-out, the concentration of chemicals that can be tolerated in the final rinse tank before poor rinse results are obtained, and the number of countercurrent cascade rinse tanks. These factors are expressed in the following equation (2):

$$V_r = \left(\frac{C_o}{C_f} \right)^{1/n} \times V_D \quad (8-1)$$

where:

V_r	=	the flow through each rinse stage, gal/min;
C_o	=	the concentration of the contaminant(s) in the initial process bath, mg/L;
C_f	=	the tolerable concentration of the contaminant(s) in the final rinse to give acceptable product cleanliness, mg/L;
n	=	the number of rinse stages used; and
V_D	=	the drag-out carried into each rinse stage, expressed as a flow, gal/min.

This mathematical rinsing model is based on complete rinsing (i.e., removal of all contaminants from the part/fixture) and complete mixing (i.e., homogeneous rinse water). Under these conditions, each additional rinse stage can reduce rinse water use by 90 percent. These conditions are not achieved unless there is sufficient residence time and agitation in each rinse tank. For less efficient rinse systems, each added rinse stage reduces rinse water use by 50 to 75 percent.

Countercurrent cascade rinsing systems have higher capital costs than overflow rinses and require more space to accommodate the additional rinse tanks. Also, when countercurrent cascade rinsing is used, the low flow rate through the rinse tanks may not provide the needed agitation for drag-out removal. In such cases, air or mechanical agitation may be added to increase rinsing efficiency.

Drag-out Rinsing

A drag-out rinse is a stagnant rinse, initially filled with fresh water, positioned immediately after the process tank. Parts are rinsed in drag-out tanks directly after exiting the process bath. The drag-out rinse collects the majority of the drag-out from the process tank, thus preventing it from entering the subsequent flowing rinses and therefore reducing pollutant loadings in those rinses. Gradually, the concentration of process chemicals in the drag-out tank rises. In the most efficient configuration, a drag-out tank follows a heated process tank that has a moderate to high evaporation rate. A portion of the fluid in the drag-out tank returns the process

tank to replace the evaporative loss. The level of fluid in the drag-out tank is maintained by adding fresh water. Electrolytic recovery of dissolved metals from drag-out tanks is also common.

Spray Rinsing

For certain part configurations, spray rinsing uses considerably less water than immersion rinsing. Spray rinsing can be performed in a countercurrent cascade configuration, further reducing water use. Spray rinsing can enhance draining over a process bath by diluting and lowering the viscosity of the process fluid film clinging to the parts.

8.1.1.2 Additional Rinse Design Elements

In addition to rinse configuration, other modifications can be made to the process line to reduce drag-out of process bath chemicals. For example, air knives and drip tanks reduce the pollutant loading and amount of rinsewater requiring treatment. Other aspects of good rinse tank design include positioning the water inlet and discharge points of the tank at opposite locations in the tank to avoid short-circuiting, using air agitation for better mixing, using a flow distributor, and using the minimum tank size possible (5). EPA describes several additional rinse design elements in more detail below.

Air Knives

Air knives are usually installed over a process tank or drip shield and are designed to remove drag-out by blowing it off the surface of parts and racks. Drag-out is routed back to the process tank. Air knives are most effective with flat parts and cannot be used to dry surfaces that passivate or stain due to oxidation.

Drip Shields

Drip shields are installed between process tanks and rinse tanks to recover process fluid dripping from racks and barrels that would otherwise fall into rinse tanks or onto the floor. Often, drip shields are an inclined piece of polypropylene or other material which is inert to the metal finishing process.

Drip Tanks

Drip tanks are similar to drag-out tanks except they are not filled with water. Parts exiting a process bath are held over the drip tank and the process fluid that drips from the parts is collected in the tank. When enough fluid is collected in the drip tank, the fluid is returned to the process tank.

Long Dwell Time

Automatic lines can be programmed to include optimum drip times. Long dwell times over the process tank reduce the volume of drag-out reaching the rinsing system. On manual lines, racks can be hung on bars over process baths to allow time to drip. Barrels can be rotated over the process bath to enhance drainage. Increases in drip time may be unsuitable for surfaces that can be oxidized or stained by exposure to air.

8.1.1.3 Rinse Water Use Control

Facilities can reduce water use by coordinating and closely monitoring rinse water requirements (e.g., rinse water use is optimized based on drag-out rates so that the rinse criterion is consistently achieved). Matching water use to rinse water requirements optimizes the quantity of rinse water used for a given work load and tank arrangement (5). Inadequate control of water-use negates the benefits of using multiple rinse tanks or employing other water conservation practices and results in a high water usage.

Many sites use some form of rinse water control. The four most common methods are flow restrictors (these can be used with other methods to regulate the rate at which water is dispensed), manual control (i.e., turning water valves on and off as needed), conductivity controls, and timer rinse controls. These are discussed below.

Flow Restrictors

A flow restrictor prevents the flow in a pipe from exceeding a predetermined flow rate. Flow restrictors are commonly installed on a rinse tank's water inlet. These devices contain an elastomer washer which flexes under pressure to maintain a constant water flow regardless of pressure. Flow restrictors can maintain a wide range of flow rates, from less than 0.1 gal/min to more than 10 gal/min. As a stand-alone device, a flow restrictor provides a constant water flow. As such, for intermittent rinsing operations, a flow restrictor does not coordinate the rinse flow with drag-out introduction. Precise control with intermittent operations typically requires a combination of flow restrictors and rinse timers. However, for continuous rinsing (e.g., continuous electroplating machines), flow restrictors may be adequate for good water use control.

Conductivity Meters

Conductivity probes measure the conductivity of water in a rinse tank to regulate the flow of fresh rinse water into the rinse system. Conductivity controllers consist of a controller, a meter with adjustable set points, a probe that is placed in the rinse tank, and a solenoid valve. As parts are rinsed, dissolved solids enter the water in the rinse tank, raising the conductivity of the water. When conductivity reaches a set point where the bath can no longer provide effective rinsing, the solenoid valve opens to allow make-up water to enter the tank. When the conductivity falls below the set point, the valve closes to discontinue the make-up water flow.

In theory, conductivity control of rinse flow is a precise method of maintaining optimum rinsing conditions in intermittently used rinse operations. In practice, conductivity controllers work best with deionized rinse water. Incoming water conductivity may vary day-to-day and season-to-season, which forces frequent set point adjustments. In addition, suspended solids and nonionic contaminants (e.g., oil) can cause inadequate rinsing and are not detected by the conductivity probe.

Rinse Timers

Rinse timers are electronic devices that control a solenoid valve. The timer usually consists of a button that, when pressed, opens the valve for a predetermined length of time, usually from 1 to 99 minutes. After the time period has expired, the valve is automatically closed. The timer may be activated either manually by the operator or automatically by the action of racks or hoists. Automatic rinse timers are generally preferred for intermittent rinses since they eliminate operator error. Rinse timers installed in conjunction with flow restrictors can provide precise control when the incoming water pressure may rise and fall. Rinse timers are less effective in continuous or nearly continuous rinse operations (e.g., continuous electroplating machines).

8.1.1.4 Pollution Prevention for Process Baths

Facilities can also implement pollution prevention technologies for process baths to reduce the pollutant loadings and therefore the amount of rinse water required. EPA gives several examples of pollution prevention technologies for process baths below.

Temperature

Temperature and viscosity are inversely related; therefore, operating at the highest possible bath temperature will lower viscosity and reduce drag-out.

Lower Concentration

Operating at the lowest possible concentration reduces the mass of chemicals in a given volume of drag-out. Also, viscosity and concentration are directly related; therefore, lower process bath concentration will result in lower viscosity and less drag-out volume. Contaminants and other process bath impurities should be minimized, if possible.

Wetting Agents

Wetting agents or surfactants may be added to some process baths to reduce viscosity and surface tension, thereby significantly reducing drag-out.

8.1.2 In-Process Pollution Prevention Technologies

This section describes in-process pollution prevention technologies used in the MP&M industry. Not all technologies discussed in this section are applicable to all MP&M sites. The pollution prevention practices that are included in the MP&M technology options are listed in Section 9.0.

In-process pollution prevention technologies can be applied to process baths or rinses. Process baths become contaminated with impurities that affect their performance. The sources of process bath contamination include: (1) breakdown of process chemicals; (2) buildup of byproducts (e.g., carbonates); (3) contamination from impurities in make-up water, chemicals, or anodes; (4) corrosion of parts, racks, tanks, heating coils, etc.; (5) drag-in of chemicals; (6) errors in bath additions; and (7) airborne particles entering the tank. If not properly maintained, process baths eventually become unusable and require disposal. Regeneration and maintenance techniques help keep baths in good operating condition, thereby extending the useful lives of process solutions. Use of these technologies reduces the pollutant loading to the wastewater treatment system, which in turn reduces wastewater treatment chemical purchases and sludge disposal costs.

This section describes the following technologies:

- C Activated carbon adsorption;
- C Carbonate freezing;
- C Centrifugation and pasteurization of machining coolants;
- C Centrifugation and recycling of painting water curtains;
- C Electrodialysis;
- C Electrolytic recovery;
- C Evaporation;
- C Filtration;
- C Ion exchange; and
- C Reverse osmosis.

8.1.2.1 Activated Carbon Adsorption

Activated carbon adsorption of electroplating baths is a common method of removing organic contaminants. Process solution flows through a filter where the carbon adsorbs organic impurities that result from the presence of oils or cleaners from the breakdown of bath constituents. Carbon adsorption can be used on either a continuous or batch basis, depending on the site's preference. Carbon treatment is most commonly applied to nickel, copper, zinc, and cadmium electroplating but can also be used to recycle paint curtain wastewater.

8.1.2.2 Carbonate “Freezing”

Carbonate “freezing” removes excessive carbonate buildup by forming carbonate salt crystals at a low temperature. This process is most often applied to electroplating baths formulated with sodium cyanide. Carbonates build up in the process bath by the breakdown of cyanide (especially at high temperatures) and the adsorption of carbon dioxide from the air. An excessive carbonate concentration reduces the quality of many metal finishing operations. Carbonate “freezing” takes advantage of the low solubility of carbonate salts in the sodium cyanide bath. The method lowers the bath temperature to approximately 26°F (-3°C), at which point hydrated salt ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) crystallizes out of solution. The crystallized carbonate can be removed by decanting the fluid into another tank or by filtration.

8.1.2.3 Centrifugation and Pasteurization of Machining Coolants

Most machining coolants consist of water-soluble oil in water. The water-soluble coolant is typically pumped through a sump, over the machining tool and part during machining, and back to the sump. Over a period of time, coolant becomes ineffective, or spent, for one or more of the following reasons:

- C The concentration of suspended solids in the coolant begins to inhibit performance;
- C Nonemulsified, or “tramp”, oil collects on the surface of the coolant;
- C The coolant becomes rancid due to microbial growth; or
- C Coolant additives are consumed by drag out and organic breakdown, thus reducing corrosion prevention and lubrication properties.

Machining coolant can be recycled using a centrifugal separator and pasteurization unit. Centrifugation removes the solids from the coolant to extend its usable life. The separator is a rotating chamber that uses centrifugal force to push the coolant through a mesh chamber, leaving behind the contaminants. Sludge is scraped from the centrifuge and collected in a sludge hopper. Some high speed centrifuges can also perform liquid - liquid separation for the removal of tramp oils. The coolant is pasteurized after separation to kill the microorganisms that cause bacterial growth. Bacterial growth can also be controlled by addition of a biocide. Figure 8-2 shows a diagram of a typical machine coolant recycling system.

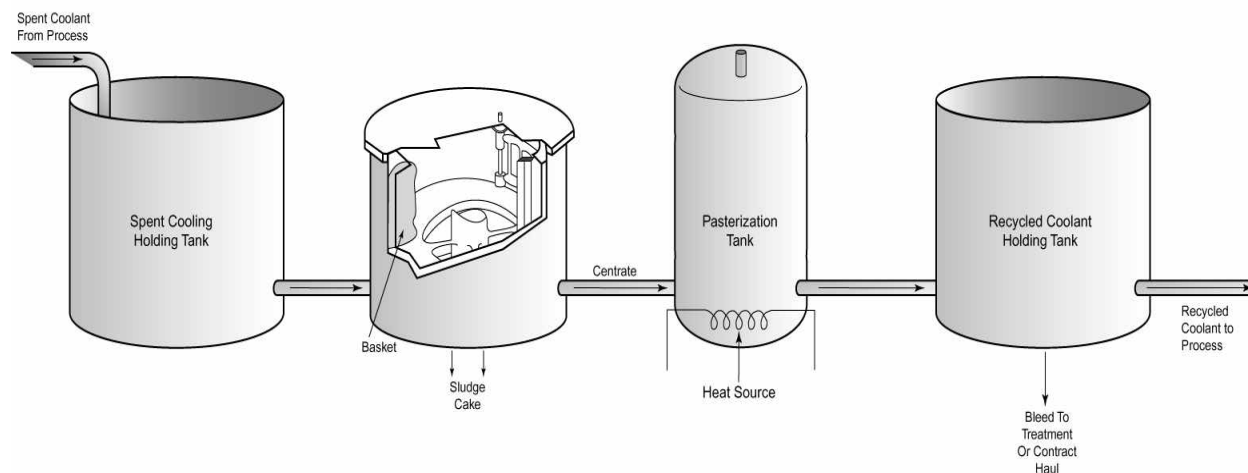


Figure 8-2. Machine Coolant Recycling System

Centrifugal separators are very reliable and require only routine maintenance, such as periodic cleaning and removal of accumulated solids. Flow rate is the primary operating factor to control. The sludge generated from this technology is commonly classified as a hazardous waste, based on the metal type processed and the amount of metal that dissolves into the coolant. The sludge is typically contract hauled for treatment and disposal.

Coolant recycling is most effective when sites minimize the number of different coolants used on site and use a centralized coolant recycling system. However, some sites may not be able to use a single recycling system because of multiple coolant types required by product or customer specifications. In this case, sites may need to purchase dedicated coolant recycling systems for each type of coolant used.

Centrifugation and pasteurization can be used along with oil skimming and biocide addition to reduce coolant discharge and pollutant generation at the source. Oil skimming using a vertical belt system removes large amounts of tramp hydraulic oils floating on the surface of the machine coolant. Oil skimming and biocide addition can further extend the life of water-soluble coolant, thereby reducing the amount of coolant and wastewater requiring treatment and disposal, and minimizing the amount of fresh coolant purchased.

8.1.2.4 Centrifugation and Recycling of Painting Water Curtains

Water curtains are a continuous flow of water behind the part being spray painted in a paint booth. The water traps paint overspray and is continuously recirculated in the paint curtain until the solids content in the wastewater necessitates either in-process treatment and recycling or discharge. Centrifugal separators remove the solids and recycle the water curtain, eliminating the need for discharge. In this system, wastewater is pumped to a holding tank, then through the centrifugal separator, which separates the solids from the wastewater (see section

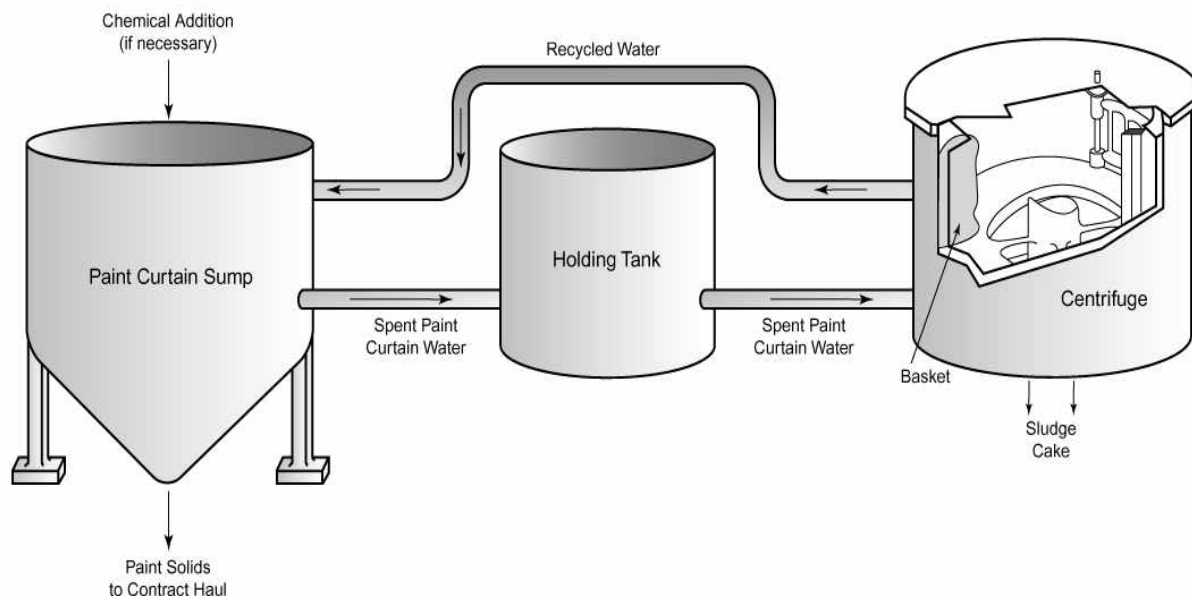


Figure 8-3. Centrifugation and Recycling of Painting Water Curtains

8.1.2.3). Solids are contract hauled for off-site disposal, while the treated wastewater is returned to the paint booth. Detactifiers may be added before centrifugation to increase the solid separation efficiency.

Centrifugation of the paint curtain proceeds until all wastewater is treated and only sludge remains in the sump. The sludge in the water curtain sump must be removed either manually, with a sludge pump, or by a vacuum truck. After the sludge has been removed and the wastewater has been treated through the centrifuge, the wastewater from the holding tank is pumped back into the water curtain sump. Make-up water is added to compensate for evaporation. Using this procedure, the paint curtain water can be continuously recycled. Figure 8-3 shows a flow diagram of a typical paint curtain centrifugation and recycling system.

Wastewater from painting water curtains commonly contains organic pollutants as well as certain metals. Eliminating the discharge of wastewater from painting water curtains may eliminate the need for an end-of-pipe treatment step for organic pollutants at certain sites. Also, if a site generates only painting wastewater and continuously recycles the wastewater, the site would not need end-of-pipe wastewater treatment.

As discussed in Section 8.1.2.3, centrifugal separators are very reliable and require only routine maintenance. Flow rate is the primary operating factor to control. One disadvantage of this technology is that it may not be economically feasible for sites generating only a small amount of paint curtain wastewater. Sites that have multiple sumps can use portable centrifuges.

The sludge generated from painting water curtains is commonly classified as a hazardous waste, based on the type of paint used, and is typically contract hauled for treatment and disposal.

8.1.2.5 Electrodialysis

Electrodialysis is a membrane technology used to remove impurities from process solutions. A direct current is applied across a series of alternating anion- and cation-exchange membranes to remove dissolved metal salts and other ionic constituents from solutions.

An electrodialysis unit consists of a rectifier and a membrane stack. The rectifier converts alternating current to direct current. The stack consists of alternating anion- and cation-specific membranes which form compartments. As the feed stream enters the unit, ions move across the electrodialysis membranes, forming a concentrated stream and a deionized stream. When the compartments are filled, a direct current is applied across each membrane in the stack. Cations traverse one cation-specific membrane in the direction of the cathode and are trapped in that concentrate compartment by the next membrane, which is anion-specific. Anions from the neighboring compartment traverse the anion-specific membrane in the direction of the anode, joining the cations, and are likewise trapped in the concentrate compartment by the next cation-specific membrane. In this way, the feed stream is depleted of ions, and anions and cations are trapped in each concentrate compartment. Electrodialysis is typically used to remove metal ions from electroplating wastewater. Figure 8-4 shows a diagram of an electrodialysis cell.

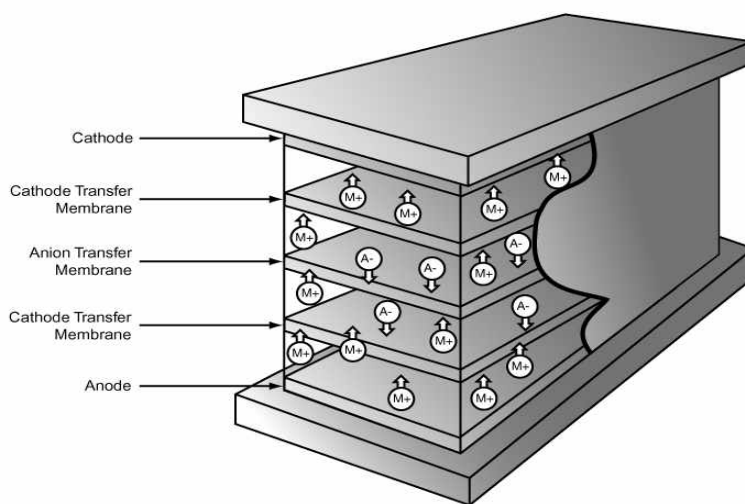


Figure 8-4. Electrodialysis Cell

8.1.2.6 Electrolytic Recovery

Electrolytic recovery is an electrochemical process used to recover metals from many types of process solutions and rinses, such as electroplating rinse waters and baths.

Electrolytic recovery removes metal ions from a waste stream by processing the stream in an electrolytic cell, which consists of a closely spaced anode and cathode. Commercial equipment consists of one or more cells, a transfer pump, and a rectifier. Current is applied across the cell and metal cations are deposited on the cathodes. The waste stream is usually recirculated through the cell from a separate tank, such as a drag-out recovery rinse.

Electrolytic recovery is typically applied to solutions containing either nickel, copper, precious metals, or cadmium. Chromium cannot be electrolytically recovered because it exists primarily in anionic forms such as dichromate. Aluminum is also a poor candidate for electrolytic recovery. Drag-out recovery rinses and ion-exchange regenerant are solutions that are commonly processed using electrolytic recovery. Some solutions require pH adjustment prior to electrolytic recovery. Acidic, metal-rich, cation regenerant is an excellent candidate stream for electrolytic recovery and is often electrolytically recovered without pH adjustment. In some cases, when the target metal concentration is reached, the waste stream may be reused as cation regenerant.

The capacity of electrolytic recovery equipment depends on the total cathode area and the maximum rated output of the rectifier. Commercial units are available with a cathode area ranging from 1 ft² to 100 ft² or larger, and an output of 10 to 1,000 amperes or more. Theoretical electrolytic recovery rates are determined by Faraday's law which states the amount of chemical change produced by an electric current is proportional to the quantity of electricity used. Theoretical recovery rates range from 1.09 grams/amp-hour for nickel to 7.35 grams/amp-hour for monovalent gold. Actual rates are usually much lower and depend on the metal concentration in the waste stream. At concentrations under 100 mg/L, electrolytic recovery rates may be below 10 percent of the theoretical maximum.

Various types of cathodes are used in electrolytic recovery units, depending mainly on the concentration of metal in the waste stream. Cathodes are often classified by their surface area. Flat-plate cathodes have the lowest surface area and are used only for recovering metal from metal-rich waste streams (usually 1,000 to 20,000 mg/L of metal). Reticulate cathodes, which have a metallized woven fiber design, have a surface area ten times greater than their apparent area. These cathodes are effective over a wide range of metal concentrations but are typically used where the dissolved metal concentration is below 100 mg/L. Carbon and graphite cathodes have the highest surface area per unit of apparent area. Their use is usually restricted to metal concentrations below 1,000 mg/L.

Dissolved metals in electrolytes can be recovered to low levels (<5 mg/L) using reticulate or carbon cathodes. In practice, however, the target concentration for most applications is 50 to 250 mg/L or higher because of the time and energy required to achieve concentrations less than 100 mg/L. With flat-plate cathodes, the target concentration is usually above 500 mg/L, because plating efficiency drops as concentration falls. Plating time required to lower the concentration of a pollutant from 100 to 10 mg/L can be several times longer than that required to lower the concentration from 10,000 mg/L to 100 mg/L. Also, unit energy costs (measured in dollars per pound of metal recovered) increase substantially at lower metal concentrations.

Labor requirements are relatively low for electrolytic recovery. Units recovering metal from drag-out recovery tanks may only require occasional cleaning and maintenance. Units treating batch discharges from ion-exchange units require more labor due to the higher metal content of the solution and the resultant increase in cathode loading frequency. Energy costs for this technology can be high, and, in some cases, exceed the recovery value of the metal. Energy requirements depend on several factors, including required voltage, rectifier efficiency, and current efficiency. In addition, from an energy standpoint, electrolytic recovery removes metals from concentrated solutions more efficiently than from dilute solutions. Electrode replacement costs may be significant for units using disposable cathodes, especially for high metal recovery rates. However, if electrodes are constructed properly, cathodes and anodes may last more than five years for most applications.

Numerous vendors offer electrolytic recovery technology. The technology is applicable to a wide range of processes, drag-out rinses, and ion-exchange regenerants due to the diversity of materials and configurations available for anodes and cathodes. Electrolytic recovery is not applicable to flowing rinses due to the lower metal concentrations and the extended time required for metal recovery. In most cases, this technology cannot cost-effectively remove dissolved metals to concentrations required for discharge to POTWs or surface waters.

8.1.2.7 Evaporation

Evaporation is a common chemical recovery technology. There are two basic types of evaporators: atmospheric and vacuum. Atmospheric evaporators are more prevalent and are relatively inexpensive to purchase and easy to operate. Vacuum evaporators are mechanically more sophisticated and are more energy-efficient. Vacuum evaporators are typically used when evaporation rates greater than 50 to 70 gallons per hour are required. There are two typical methods of in-process evaporation and reuse: 1) evaporate the water and then condense the water for reuse in baths and rinses, and 2) evaporate the water and reuse the concentrate (i.e., the process solution that remains after water is evaporated) in process baths. Reusing the condensate is more common.

8.1.2.8 Filtration

Filtration removes suspended solids from surface finishing solutions. Suspended solids in surface finishing solutions may cause roughness and burning of deposits. Filtration uses various types of equipment, the most common of which are cartridge filters, precoat diatomaceous earth filters, sand, and multimedia filters. Cartridge filters are available with either in-tank or external configurations. The in-tank units are used mostly for small tanks and the external units for larger tanks. Most cartridges are disposable; however, washable and reusable filters are available, which further reduce waste generation. Precoat, sand, and multimedia filters are used mostly for large tanks. The filter media used depends on the chemical composition of the bath. All filtration systems are sized based on solids loading and the required flow rate.

Membrane filtration can also be used to remove oils and metals from process baths or rinses. Membrane filters can be used to recycle paint curtain or machine coolant wastewater and are typically used to recover and recycle electrophoretic painting (“e-coat”) solutions. Membrane filtration is a pressure-driven process used to separate solution components based on molecular size and shape. Solvent and small solutes can pass through the membrane while the membrane retains and collects larger compounds as a concentrated waste stream. The cleaner permeate can be reused in the process. Figure 8-5 shows a typical membrane filtration unit.

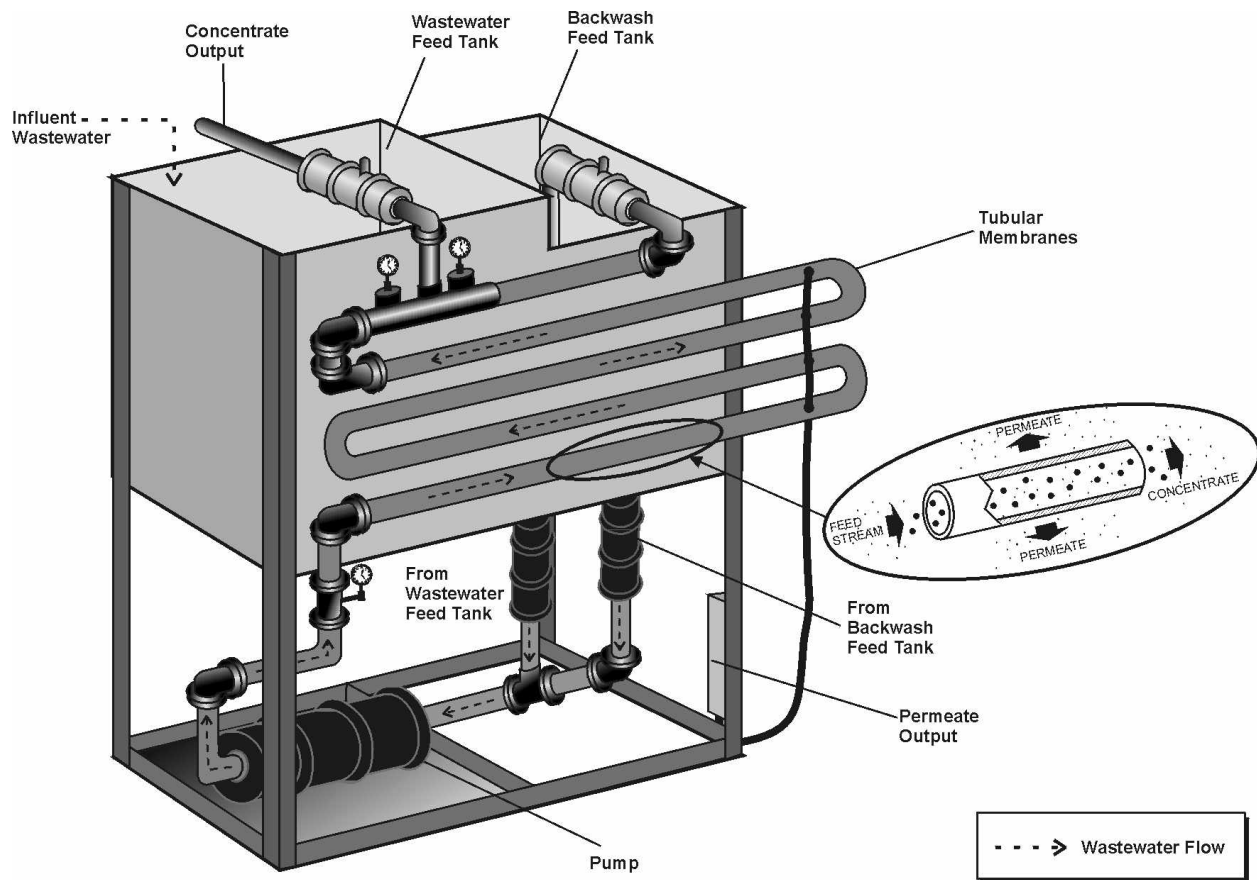


Figure 8-5. Membrane Filtration Unit

8.1.2.9 Ion Exchange (in-process)

Ion exchange is a commonly used technology within the MP&M industry. In addition to water recycling and chemical recovery applications, ion exchange is used to soften or deionize raw water for process solutions. Figure 8-6 shows a typical ion exchange system.

Ion exchange is a reversible chemical reaction that exchanges ions in a feed stream for ions of like charge on the surface of an ion-exchange resin. Resins are broadly divided into cationic or anionic types. Typical cation resins exchange H^+ for other cations, while anion resins exchange OH^- for other anions.

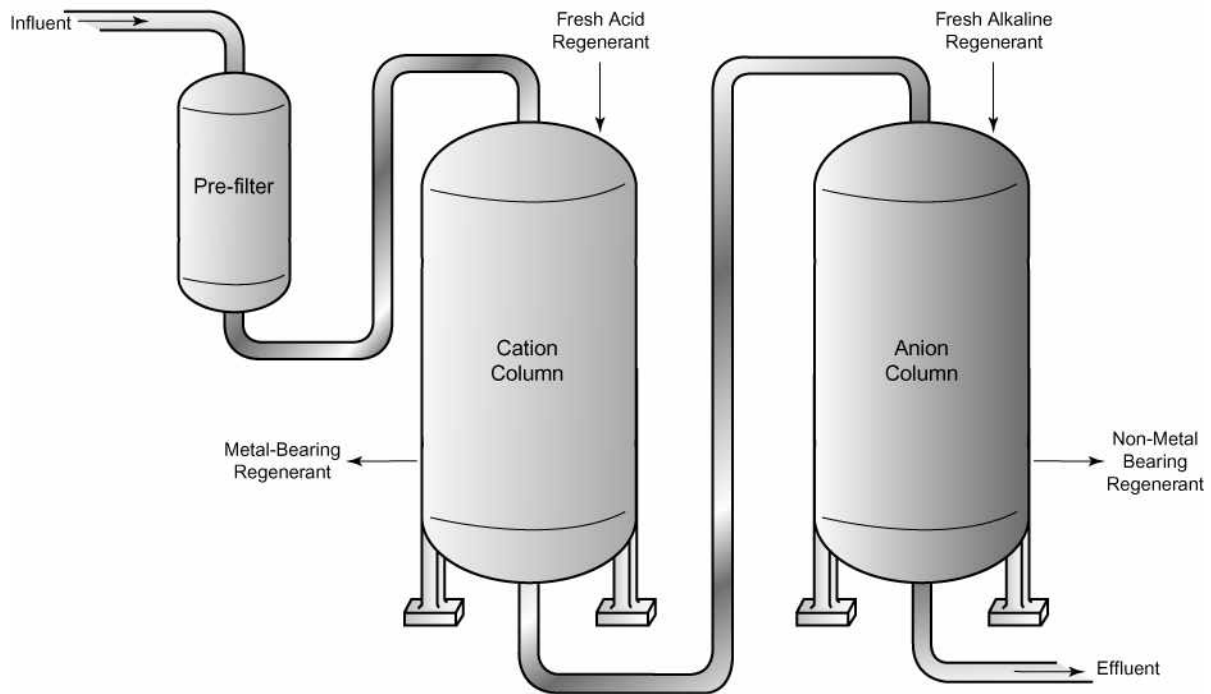


Figure 8-6. Ion Exchange

In practice, a feed stream passes through a column, which holds the resin. The feed stream is usually either dilute rinse water (in-process ion exchange) or treated wastewater (end-of-pipe ion exchange). Often, prior to ion-exchange treatment, the feed stream passes through a cartridge filter and a carbon filter to remove suspended solids and organics that foul the resin bed. The exchange process continues until the capacity of the resin is reached (i.e., an exchange has occurred at all the resin sites). A regenerant solution is then passed through the column. For cation resins, the regenerant is an acid, and the H^+ ions replace the cations captured from the feed stream. For anion resins, the regenerant is a base, and OH^- ions replace the anions captured from the feed stream. The metals concentration is much higher in the regenerant than in the feed stream; therefore, the ion-exchange process not only separates the metals from the wastestream but also results in a more concentrated wastestream.

Ion exchange is used for water recycling and/or metal recovery. For water recycling, cation and anion columns are placed in series. The feed stream is deionized and the product water is reused for rinsing. Often, closed-loop rinsing is achieved. The regenerant from the cation column contains metal ions, which can be recovered in elemental form via electrolytic recovery (see Section 8.1.2.6). The anion regenerant is typically discharged to wastewater treatment. This type of ion exchange is used to recycle relatively dilute rinse streams. Generally, the total dissolved solids (TDS) concentration of such streams must be below 500 mg/L to maintain an efficient regeneration frequency. Reducing drag-out can enhance the efficiency of the recovery process. Effluent TDS concentrations of 2 mg/L or less are typical.

When metal recovery is the only objective, a single or double cation column unit containing selective resin is used. These resins attract divalent cations while allowing monovalent cations to pass, a process usually called metal scavenging. This technology is efficient if the metal ions being scavenged are the primary source of ions in the stream. Ion exchange provides effective metals recovery even when the metal content of the stream is only a small fraction of the TDS present in the stream, making scavenging suitable over a wider range of TDS than water recycling. Scavenging also provides a highly concentrated regenerant, particularly suitable for electrolytic recovery (see Section 8.1.2.6). Water recycling using this ion exchange configuration is not possible since only some of the cations and none of the anions are removed. Standard units typically achieve effluent metal concentrations of under 0.5 mg/L.

Many process wastewaters are excellent candidates for ion exchange, including the rinse water from plating processes of chromium, copper, cadmium, gold, lead, nickel, tin, tin-lead, and zinc. Ion exchange resins are usually regenerated using inexpensive chemicals such as sulfuric acid and sodium hydroxide. Gold-bearing resins are difficult to regenerate and frequently require incineration to recover the gold content. Lead is also difficult to recover from ion exchange resins. Methane sulfonic acid and fluoboric acid (usually not suitable for electrolytic recovery) are effective regenerants for lead ion exchange but are very expensive. Cyanide rinse waters are amenable to ion exchange; cation resins are capable of breaking the metal-cyanide complex and the cyanide is removed in the anion column. The metals in the cation regenerant can be electrolytically recovered and the cyanide present in the anion regenerant can be returned to the process or discharged to treatment.

Ion-exchange equipment ranges from small, manual, single-column units to multi-column, highly automated units. Two sets of columns are necessary for continuous treatment; one set receives the wastewater flow while the other set is being regenerated. Thus, two-column metal scavenging and four-column deionizing systems are common. Automatic systems direct the wastewater flow and initiate regeneration with little or no operator involvement.

The labor requirements for ion exchange depend on the automation level of the equipment. Manual systems can have significant labor costs associated with preparing, transporting, and disposing of regenerants. Automatic systems require far less labor. Resins need to be replaced periodically due to organic contamination, resin oxidation, and fouling from suspended solids. This process can be hastened by misuse, accidents, or poor engineering.

Equipment size is based on flow rate and concentration. Resin capacity varies but often ranges from 1 to 2 lbs/ft³. Flow rates may range from 1 to 20 or more gpm. Columns are typically sized to handle wastewater flow for at least a period of time equal to that required for regeneration. Automatic systems are sized to provide continuous treatment. Regeneration volume typically ranges from 2 to 4 resin bed volumes of dilute acid or caustic. Concentrations of feed stream contaminants generally range from 10 to 20 g/L.

8.1.2.10 Reverse Osmosis

Reverse osmosis is a membrane separation technology used by the MP&M industry for chemical recovery. Dilute rinse water is pumped to the surface of the reverse osmosis membrane at pressures of 400 to 1,000 pounds per square inch gauge (psig). The membrane separates the feed stream into a reject stream and a permeate. The reject stream, containing most of the dissolved solids in the feed stream, is deflected from the membrane while the permeate passes through. Reverse osmosis membranes reject more than 99 percent of multivalent ions and 90 to 96 percent of monovalent ions, in addition to organics and nonionic dissolved solids. The permeate stream is usually of sufficient quality to be recycled as rinse water, despite the small percentage of monovalent ions (commonly potassium, sodium and chloride) that pass through the membrane. Reverse osmosis equipment is similar to the equipment shown in Figure 8-5.

A sufficiently concentrated reject stream can be returned directly to the process bath. The reject stream concentration can be increased if the stream is recycled through the unit more than once or by increasing the feed pressure. In multiple-stage units containing more than one membrane chamber, the reject stream from the first chamber is routed to the second, and so on. The combined reject streams from multistage units may, in some cases, have high enough concentrations to be returned directly to the bath.

The capacity of reverse osmosis equipment is generally measured in flow volume, and is determined by the membrane surface area and operating pressure. Generally, increasing the surface area of the membrane increases the capacity. Operating at higher pressures increases

the permeate flow volume per unit membrane area (also called the flux). Reject stream concentration increases with pressure and decreases as flow volume increases.

Facilities may need to prefilter and pretreat the feed stream to lengthen membrane life or reduce the frequency of fouling; filtration to remove suspended solids is usually necessary. Adjusting pH may prevent precipitation as the feed stream is concentrated, but it may make the concentrate unfit to return to the process bath.

Reverse osmosis is most applicable to electroplating rinse waters, including electroplating of Watts nickel, bright nickel, brass cyanide, copper cyanide, and zinc cyanide. This technology can treat TDS concentrations of up to 1,000 mg/L. Permeate TDS concentrations of 250 mg/L or less are typical, and the dissolved solids are mostly common monovalent ions, allowing the permeate stream to be reused in many rinsing operations.

The maximum achievable reject stream concentration for basic reverse osmosis equipment is approximately 20,000 mg/L TDS. Multipass and multistage units achieve concentrations of 30,000 mg/L TDS or higher. If the reject stream is acceptable to return directly to the process bath and the permeate is recycled as rinse water, a closed loop is created. However, returning the reject stream directly to the bath is uncommon because the concentration is often too low. In cases where the reject stream concentration is not high enough to return it to the bath, it can be concentrated with an evaporator, electrolytically recovered, or treated conventionally (e.g., with chemical precipitation). When evaporators are used, however, reverse osmosis loses its low-energy advantage over other in-process reuse and recovery technologies.

When both technologies include an electrolytic recovery unit, reverse osmosis often has a higher capital cost than ion exchange. As end-of-pipe treatment, reverse osmosis and ion exchange both remove similar quantities of metals; however, reverse osmosis may allow for more water recycling. During reverse osmosis, energy is consumed only by pumps. In most cases, water is recycled; in some cases, a closed loop is possible. Compared to ion exchange, reverse osmosis can treat somewhat higher feed stream concentrations. The concentration of reverse osmosis reject streams are near or higher than that of ion-exchange regenerants. Both are less effective in handling oxidizing chemistries or feed streams high in organics and total suspended solids (TSS). Ion-exchange effluent generally has a lower TDS concentration than reverse osmosis permeate and can be recycled in most rinses.

For most applications, reverse osmosis membranes last for one to five years, although they are susceptible to fouling from organics, suspended solids, or misuse. Reverse osmosis units may have instrumentation that indicates the condition of the membrane by measuring the flux. If the membrane fouls or clogs, the flux rate drops, indicating that the membrane should be cleaned. Labor associated with operating reverse osmosis equipment is for periodic membrane cleaning. Membrane and pump replacement are the primary maintenance items.

8.1.3 Other Types of Pollution Prevention Practices

Many other types of pollution prevention practices are performed at MP&M facilities including the following: training and supervision; production planning; process or equipment modification; raw material and product substitution or elimination; loss prevention and housekeeping; waste segregation and separation; and closed-loop recycling. EPA describes each of these practices below. Some of these practices may be elements of an Environmental Management System (EMS).

Training and Supervision. Training and supervision ensure that employees are aware of, understand, and support the company's pollution prevention goals. Effective training programs translate these goals into practical information that enables employees to minimize waste generation by properly and efficiently using tools, supplies, equipment, and materials.

Production Planning. Production planning can minimize the number of process operation steps and eliminate unnecessary procedures (e.g., planning production can eliminate additional cleaning steps between process operations).

Process or Equipment Modification. Sites can modify processes and equipment to minimize the amount of waste generated (e.g., changing rack configuration to reduce drag-out).

Raw Material and Product Substitution or Elimination. Where possible, sites should replace toxic or hazardous raw materials or products with other materials that produce less waste and/or less toxic waste (e.g., replacing chromium-bearing solutions with nonchromium-bearing and less toxic solutions, or consolidating types of cleaning solutions and machining coolants).

Loss Prevention and Housekeeping. Loss prevention and housekeeping includes performing preventive maintenance and managing equipment and materials to minimize leaks, spills, evaporative losses, and other releases (e.g., inspecting the integrity of tanks on a regular basis; using chemical analyses instead of elapsed time or number of parts processed as the basis for disposal of a solution).

Waste Segregation and Separation. Sites should avoid mixing different types of wastes or mixing hazardous wastes with nonhazardous wastes. Similarly, sites should not mix recyclable materials with noncompatible materials or wastes. For example, MP&M facilities can segregate scrap metal by metal type, separate cyanide-bearing wastewater for preliminary treatment, and segregate coolants for recycling or treatment.

Closed-Loop Recycling. MP&M sites can recover and reuse some process streams. For example, some sites can use ion exchange to recover metal from electroplating rinse water, the rinsewater can be reused, and the regenerant solution can be used as solution make-up.

8.2 Preliminary Treatment of Segregated Wastewater Streams

Preliminary treatment systems reduce pollutant loadings in segregated waste streams prior to end-of-pipe treatment. Wastewater containing pollutants such as cyanide, hexavalent chromium, oil and grease, or chelated metals inhibit the performance of end-of-pipe treatment systems and require preliminary treatment. Proper segregation and treatment of these streams is critical for the successful treatment of MP&M wastewater. Highly concentrated metal-bearing wastewater may also be treated to reduce metal concentrations before end-of-pipe treatment. This section describes the following wastewater streams that typically undergo preliminary treatment at MP&M facilities:

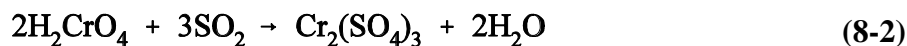
- C Chromium-bearing wastewater;
- C Concentrated metal-bearing wastewater;
- C Cyanide-bearing wastewater;
- C Chelated metal-bearing wastewater; and
- C Oil-bearing wastewater.

8.2.1 Chromium-Bearing Wastewater

MP&M facilities generate hexavalent-chromium-bearing wastewater from acid treatment, anodizing, conversion coating, and electroplating operations and rinses. Hexavalent chromium exists in an ionic form and does not form a metal hydroxide; therefore, this wastewater is not treated directly by chemical precipitation and sedimentation. The wastewater requires preliminary chemical treatment to reduce the hexavalent chromium to trivalent chromium. The trivalent chromium can then be removed by chemical precipitation and sedimentation. The chemical reduction process is discussed below. Figure 8-7 presents a process flow diagram of a continuous chromium reduction system.

Reduction is a chemical reaction in which electrons are transferred from one chemical (the reducing agent) to the chemical being reduced. Sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate form strong reducing agents in water. MP&M facilities use these reducing agents to reduce hexavalent chromium to the trivalent form, which allows the metal to be removed from solution by subsequent chemical precipitation.

Sodium metabisulfite, sodium bisulfite, and sulfur dioxide are the most widely used reducing agents at MP&M sites. Below is an equation showing the sulfur dioxide reaction (reduction using other reagents is chemically similar):



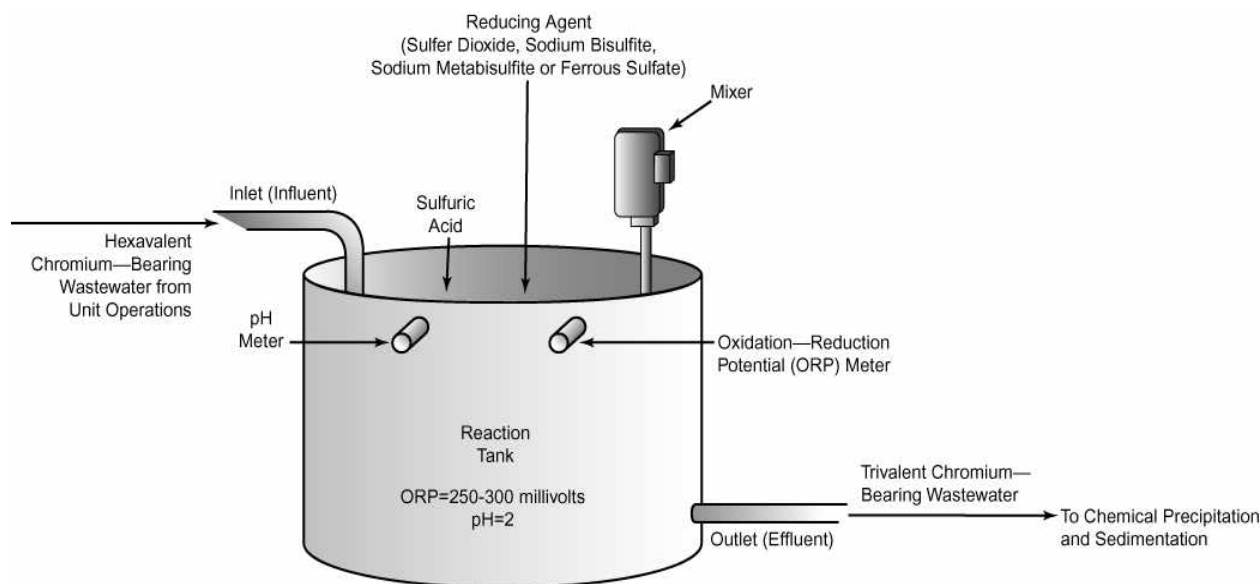


Figure 8-7. Chemical Reduction of Hexavalent Chromium

An operating pH of between 2 and 3 is normal for chromium reduction. At pH levels above 5, the reduction rate is slow, and oxidizing agents such as dissolved oxygen and ferric iron interfere with the reduction process by consuming the reducing agent.

Typically, the chemicals are retained in a reaction tank for 45 minutes. The tank is equipped with pH and oxidation-reduction potential (ORP) controls. Sulfuric acid is added to maintain a pH of approximately 2, and a reducing agent is metered to the reaction tank to maintain the ORP at 250 to 300 millivolts.

Chemical reduction of hexavalent chromium is a proven technology that is widely used at MP&M sites. Operation at ambient conditions requires little energy, and the process is well suited to automatic control. For high concentrations of chromium, treatment chemical costs may be significant.

Maintenance of chemical reduction systems consists of sludge removal, the frequency of which depends on the concentration of contaminants. There may also be small amounts of sludge generated due to minor shifts in the solubility of the contaminants (e.g., iron hydroxides). This sludge can be removed by the sludge-handling equipment associated with the chemical precipitation system.

8.2.2 Concentrated Metal-Bearing Wastewater

Concentrated metal-bearing wastewater from spent process solutions can be slowly metered to the end-of-pipe chemical precipitation system and commingled with other facility wastewater or batch treated. Some facilities send concentrated metal-bearing wastewater for off-site treatment rather than treating the wastewater on site. Batch treatment of concentrated metal-bearing wastewater provides better control of the treatment system (e.g., the treatment chemicals can be better tailored to the specific solution being treated), better treatment of difficult-to-treat materials (e.g., photo resist-bearing wastewater), and potential recovery of metals from the sludge. With batch treatment, effluent from the batch treatment tank is typically discharged to the end-of-pipe treatment system for additional polishing.

Batch chemical precipitation of concentrated metal-bearing wastewater typically occurs in a single stirred tank, where a precipitating agent (e.g., sodium hydroxide, lime, sodium sulfide) is added to create an insoluble metal hydroxide or sulfide complex. Following precipitate formation, a polyelectrolyte is added to flocculate the metal hydroxide or metal sulfide particles into larger clumps that will settle to the bottom of the reaction tank following mixing. Clarified effluent from the batch tank is discharged to the end-of-pipe treatment system and the settled sludge, typically containing only one type of metal, is transferred offsite for metals recovery.

8.2.3 Cyanide-Bearing Wastewater

Plating and cleaning wastewater may contain significant amounts of cyanide, which should be destroyed through preliminary treatment. In addition to its toxicity, cyanide forms complexes with metals that prohibit subsequent removal in chemical precipitation systems. Cyanide is typically destroyed using alkaline chlorination with sodium hypochlorite or chlorine gas or by ozone oxidation. EPA describes these two processes below.

8.2.3.1 Alkaline Chlorination

Cyanide destruction through alkaline chlorination is widely used in industrial wastewater treatment. Chlorine is typically used as either chlorine gas or sodium hypochlorite (i.e., bleach). This process is shown by the following two-step chemical reaction:

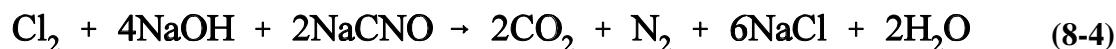


Figure 8-8 presents a process flow diagram showing alkaline chlorination of cyanide.

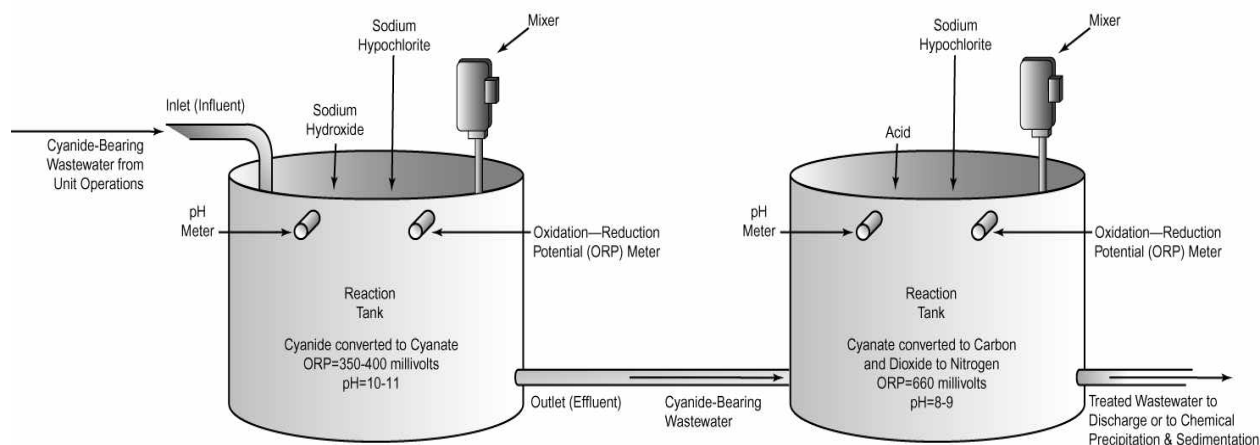


Figure 8-8. Cyanide Destruction Through Alkaline Chlorination

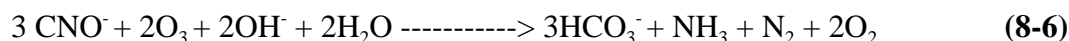
The alkaline chlorination process oxidizes cyanides to carbon dioxide and nitrogen. The equipment often consists of an equalization tank followed by two continuous reaction tanks, although the batch reaction can be conducted in a single tank. Each tank has an electronic controller to monitor and maintain the required pH and ORP. To oxidize cyanides to cyanates, chlorine or sodium hypochlorite is metered to the reaction tank as necessary to maintain the ORP at 350 to 400 millivolts, and aqueous sodium hydroxide is added to maintain a pH of 10 to 11. In the second reaction tank, the ORP and the pH level are typically maintained at 600 millivolts and 8 to 9, respectively, to oxidize cyanate to carbon dioxide and nitrogen. Each reaction tank has a chemical mixer designed to provide approximately one turnover per minute. The batch process is usually conducted by using two tanks, one to collect water over a specified time period and one to treat an accumulated batch. If concentrated wastes are frequently dumped, another tank may be required to equalize the flow to the treatment tank. When the holding tank is full, the liquid is transferred to the reaction tank for treatment.

Alkaline chlorination can be performed at ambient temperature, can be automatically controlled at relatively low cost, and can achieve effluent concentrations of free cyanide that are below the detection limit. Disadvantages include the need for careful pH control, possible chemical interference in treating mixed wastes, and the potential hazard of storing and handling chlorine gas (if sodium hypochlorite is not used). If organic compounds are present, chlorinated organics may be generated. This technology is not effective in treating metalocyanide complexes, such as ferrocyanide.

8.2.3.2 Ozone Oxidation

A less common cyanide treatment method is ozone oxidation. Ozone, generated as a gas, is bubbled through a wastewater solution containing free cyanide. Part of the ozone in

the gas phase is transferred to the solution, where it reacts with cyanide, converting it to cyanate. Additional ozone reacts with the cyanate to convert it to nitrogen gas, ammonia, and bicarbonate, as shown by the reaction below.



The reaction rate is limited by mass transfer of ozone to the liquid, the cyanide concentration, and temperature. Literature data show that amenable cyanide in electroplating wastewaters can be reduced to below detection using the oxidation process. Ozone is not effective in treating metallocyanide complexes, such as ferrocyanide, unless ultraviolet light is added to the reaction tank.

One advantage ozone has over chlorine is the type of residuals formed. Chlorine oxidation of organic compounds has the potential to form trihalomethanes. Ozone oxidizes organic compounds to form relatively less toxic, short-chain organic acids, ketones, and aldehydes. Equipment required for ozone oxidation of cyanides includes an ozone generator, gas diffusion system, a mixed reaction tank, and off-gas controls to prevent the release of unreacted ozone.

The major disadvantage of the ozone oxidation process is the capital and operating cost. Ozone must be manufactured on site and delivered directly to the reaction tank. Ozone generation equipment is expensive, and facilities must also purchase closed reaction tanks and ozone off-gas treatment equipment.

8.2.4 Chelated Metal-Bearing Wastewater

Certain MP&M wastewater contains chelating agents that form metal complexes and interfere with conventional chemical precipitation processes. This wastewater is often associated with electroless plating, and requires specific treatment for the chelated metals. In general, there are three methods of treating these wastewaters:

- C Reduction to elemental metal;
- C Precipitation as an insoluble compound; and
- C Physical separation.

8.2.4.1 Reduction to Elemental Metal

Reduction to elemental metal can be done using one of two methods. One method is electrolytic recovery (see Section 8.1.2.6), in which the dissolved metal is deposited on a cathode for reclamation or disposal. The electric current provides the electrons to reduce the metal ion to its elemental form. The reaction rate and achievable concentration for this

technology depend on the volume of wastewater per unit surface area of cathode. This method typically does not lower metal concentrations enough for wastewater discharge.

The second method uses a reducing agent to provide the electrons to reduce the metal. Possible reducing agents for use in chelated wastewater streams include:

- C Sodium borohydride;
- C Hydrazine; and
- C Sodium hydrosulfite.

Upon reduction, the metal forms a particulate in solution, which can then be removed by conventional solids removal techniques. To be used effectively these reducing agents sometimes require the use of other chemicals for pH adjustment. Figure 8-9 presents a flow diagram showing this method of chemical reduction of chelated metals.

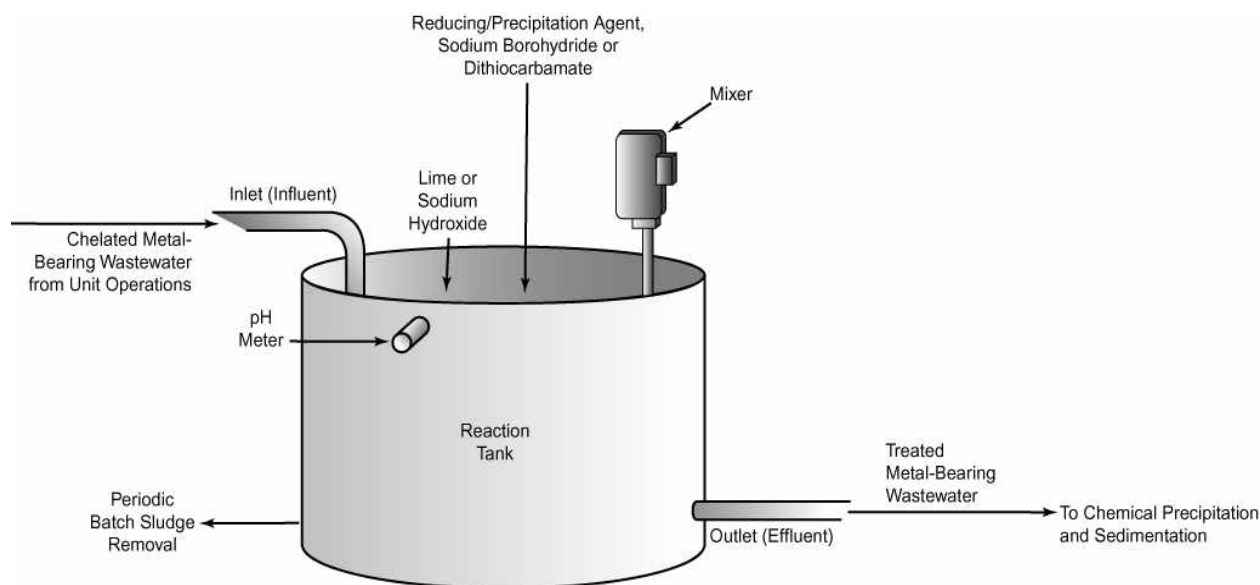


Figure 8-9. Chemical Reduction / Precipitation of Chelated Metals

8.2.4.2 Precipitation of an Insoluble Compound

The presence of chelating agents hinders the formation of hydroxides, making hydroxide precipitation ineffective on chelated metal-bearing wastewaters. Other precipitation methods that are less affected by chelating agents include sulfide precipitation, dithiocarbamate (DTC) precipitation, and carbonate precipitation. Except for DTC precipitation, all of these technologies are discussed in Section 8.3. DTC is added to solution in stoichiometric ratio to the metals present. DTC is effective in treating chelated wastewater; however, DTC compounds are also a class of pesticides and, if used incorrectly, may cause process upsets in the biological treatment used at a POTW and can potentially be harmful to the environment (e.g., lead to fish

kills if DTC passes through the POTW and reaches surface waters). In addition to DTC's potential toxic effects when misused, another disadvantage is DTC precipitation generates large amounts of sludge.

8.2.4.3 Physical Separation

Ion exchange and reverse osmosis can separate metals from solution. These technologies are not affected by chelating agents in the wastewater, making them effective in treating wastewater from electroless plating. These technologies are discussed in section 8.1.2.9 and 8.1.2.10, respectively.

8.2.5 Oil-Bearing Wastewater

Some MP&M wastewater (e.g., alkaline cleaning wastewater and water-based metal-working fluids) contains significant amounts of oil and grease. This wastewater sometimes requires preliminary treatment to remove oil and grease and organic pollutants. Oil/water separation includes the breaking of oil/water emulsions as well as the gravity separation of oil. When only free oil (i.e., non-emulsified oil) is present, only oil skimming is necessary for effective treatment. Techniques available to remove oil include chemical emulsion breaking followed by oil/water separation or dissolved air flotation, oil skimming, and ultrafiltration. EPA describes these technologies in more detail below.

8.2.5.1 Chemical Emulsion Breaking

Chemical emulsion breaking is used to break stable oil/water emulsions (oil dispersed in water, stabilized by electrical charges and emulsifying agents). A stable emulsion will not separate or break down without chemical and or physical treatment. Chemical emulsion breaking is applicable to wastewater containing emulsified coolants and lubricants such as machining and grinding coolants and impact and pressure deformation lubricants. This technology is also applicable to cleaning solutions that contain emulsified oils. Figure 8-10 shows a flow diagram of a type of continuous chemical emulsion breaking system.

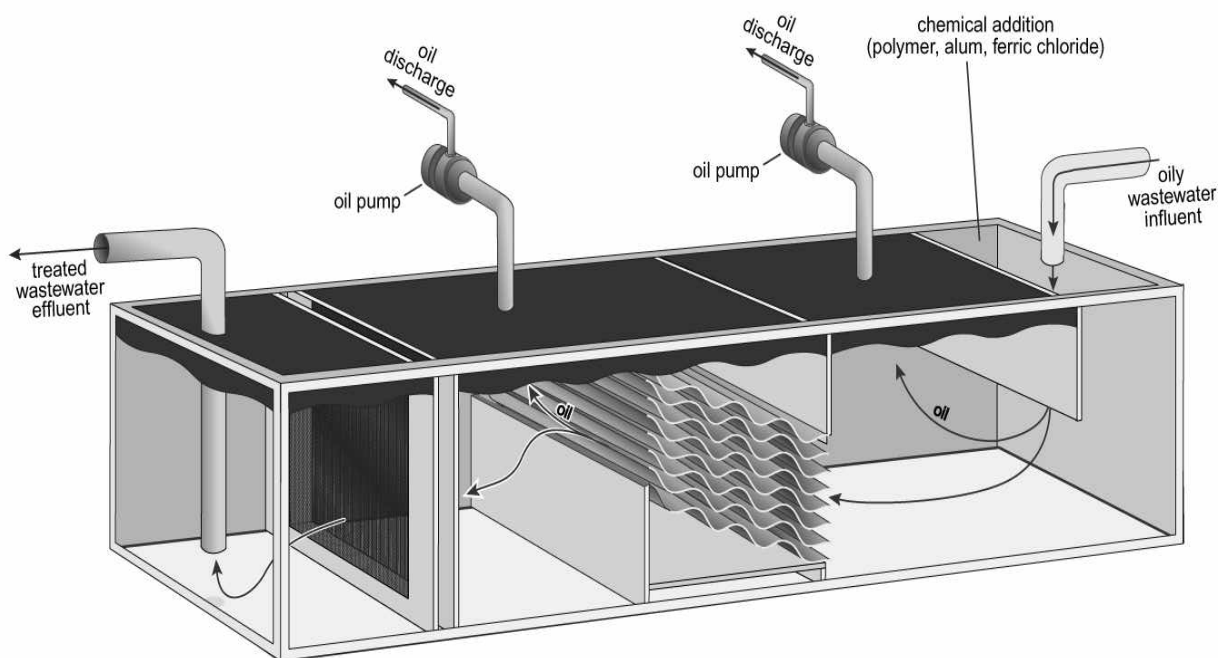


Figure 8-10. Continuous Chemical Emulsion Breaking Unit with Coalescing Plates

Treatment of spent oil/water emulsions involves adding chemicals to break the emulsion followed by oil/water separation. The major equipment required for chemical emulsion breaking includes reaction chambers with agitators, chemical storage tanks, chemical feed systems, pumps, and piping. Factors to be considered for destroying emulsions are type of chemicals, dosage and sequence of addition, pH, mixing, heating requirements, and retention time.

Chemicals (e.g., polymers, alum, ferric chloride, and organic emulsion breakers) break emulsions by neutralizing repulsive charges between particles, precipitating or salting out emulsifying agents, or weakening the interfacial film between the oil and water so it is readily broken. Reactive cations (e.g., H^+ , Al^{+3} , Fe^{+3}) and cationic polymers are particularly effective in breaking dilute oil/water emulsions. Once the charges have been neutralized or the interfacial film broken, the small oil droplets and suspended solids either adsorb on the surface of the floc that is formed, or break out and float to the top. Different types of emulsion-breaking chemicals are used for different types of oils. If more than one chemical is required, the sequence of adding the chemicals can affect both breaking efficiency and chemical dosages.

Another important consideration in emulsion breaking is pH, especially if cationic inorganic chemicals, such as alum, are used as coagulants. For example, a pH of between 2 and 4 keeps the aluminum ion in its most positive state where it most effectively neutralizes charges. After some of the oil is broken free and skimmed, raising the pH into the 6-to-8 range with lime

or caustic causes the aluminum to hydrolyze and precipitate as aluminum hydroxide. This floc entraps or adsorbs destabilized oil droplets, which can then be separated from the water. Cationic polymers can break emulsions over a wider pH range and thus avoid acid corrosion and the additional sludge generated from neutralization; however, this process usually requires adding an inorganic flocculent to supplement the adsorptive properties of the polymer emulsion breaker.

Mixing is important in effectively breaking oil/water emulsions because it provides proper chemical feed and dispersion. Mixing also causes droplets to collide and break the emulsion and promotes subsequent agglomeration into larger droplets. Heating also improves chemical emulsion breaking by lowering the viscosity and increasing the apparent specific gravity differential between oil and water. In addition, heating increases the frequency of droplet collisions, which helps to rupture the interfacial film.

Once an emulsion is broken, the oil floats to the surface of the water because of the difference in specific gravities between the oil and the water. Solids usually form a layer between the oil and water, since some solids become suspended in the oil. The longer the retention time, the more complete the separation between the oil, solids, and water. Oils and solids are typically skimmed from the surface of the water in a subsequent step after chemical emulsion breaking. Often, other techniques, such as air flotation or rotational separation (e.g., centrifugation), are used to enhance separation after chemical emulsion breaking.

The advantages of chemical emulsion breaking are the high removal efficiency potential and the possibility of reclaiming the oily waste. Disadvantages include corrosion problems associated with acid-alum systems, operator training requirements for batch treatment, chemical sludges produced, and poor efficiency for low oil concentrations.

Chemical emulsion breaking is a very reliable process. The main control parameters are pH and temperature. Maintenance is required on pumps, mixers, instrumentation and valves, and periodic cleaning of the treatment tank is required to remove any accumulated solids. Energy use is typically limited to mixers and pumps, but can also include heating. Solid wastes generated by chemical emulsion breaking include surface oil and oily sludge, which are usually contract hauled for disposal by a licensed contractor. If the recovered oil contains a low enough percentage of water, it may be burned for its fuel value or processed and reused.

8.2.5.2 Oil Skimming

Oil skimming is a physical separation technology that removes free or floating oil from wastewater using the difference in specific gravity between oils and water. Common separation devices include belts, rotating drums, disks, and weir oil skimmers and coalescers. These devices are not suited to remove emulsified oil, which requires chemical treatment, membrane filtration, or other treatment. Figures 8-11a and 8-11b show flow diagrams of disc and belt oil skimming units, respectively, that can be used for small systems or on process tanks. The oil removal system shown in Figure 8-10 is used for large systems.

To separate oil from process solutions, oil skimming devices are typically mounted onto the side of a tank and operated on a continuous basis. The disk skimmer is a vertically rotating disk that is partially submerged in the solution (see Figure 8-11a). The disk continuously revolves between spring-loaded wiper blades that are located above the liquid surface. The disk's adhesive characteristics cause the floating oil to remain on the disk. As the disk's surface passes under the wiper blades, the oil is scraped off and diverted to a run-off spout

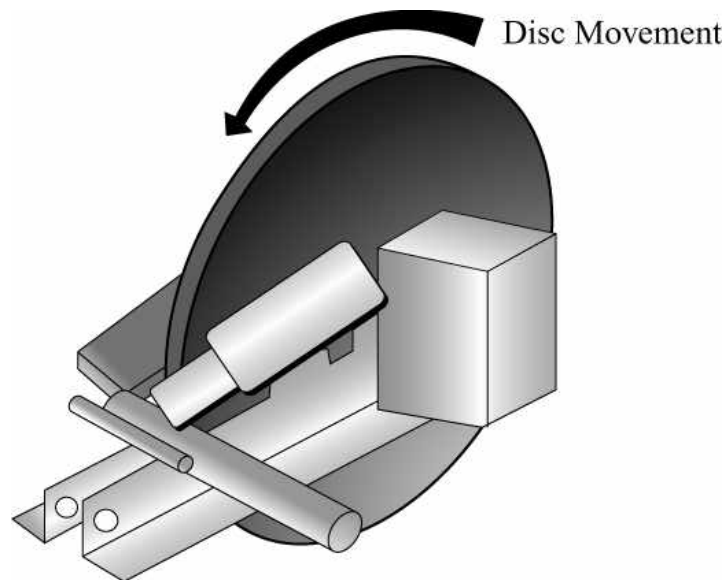


Figure 8-11a. Disc Oil Skimming Unit

for collection. Belt (see figure 8-11b) and drum skimmers operate in a similar manner, with either a continuous belt or drum rotating partially submerged in a tank. As the surface of the belt or drum emerges from the liquid, the oil that adheres to the surface is scraped off (drum) or squeezed off (belt) and diverted to a collection vessel. The oil is typically contract hauled for disposal.

Gravity separators use overflow and underflow weirs to skim a floating oil layer from the surface of the wastewater. A weir allows the oil layer to flow over the weir into a trough for disposal or reuse while most of the water flows underneath the weir. A diffusion device, such as a vertical slot weir, helps create a uniform flow through the system and increase oil removal efficiency.

A skimmer's removal efficiency depends on the composition of the waste stream and the retention time of the water in the tank. Larger, more buoyant particles require less retention time than smaller particles. The retention time necessary for phase separation and subsequent skimming varies from 1 to 15 minutes, depending on the wastewater characteristics.